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(54) LUBRICANT ADDITIVES

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ERRATA

SPECIFICATION No. 1,372,532

- Page 1, lines 40 to 45, *delete* whole lines
 Page 4, lines 34 to 40, *delete* whole lines
 Page 5, line 55, *for* 0—100 *read* 0—10
 Page 5, line 70, Table I, above columns 2
 and 3, *insert* Mixture composition
 Page 6, line 28, *after* acids *insert* present in
 the mixture obtained to alkylphenols and
 alkylsalicylic acids

THE PATENT OFFICE
 5th March, 1976

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atoms and an alkaline earth metal, in particular calcium is present, have been used for many years in engines, in particular diesel engines. These additives have dispersing properties enabling them to keep the internals of engine cylinders clean and to counteract the deposition of carbonaceous products on pistons and in ring grooves, ring-sticking thus being prevented.

Recently the said lubricating oils have increasingly been used in gasoline engines. It has been found that in gasoline engines the protection against rusting, with lubricating oils which contain the said salts of alkylsalicylic acids, is not in all cases completely adequate. Consequently, lubricant additives have been searched for by which the above drawback can be overcome.

It has appeared that lubricating oils in which mixtures of salts of alkylsalicylic acids, is not in all cases completely adequate. Consequently, lubricant additives have been searched for by which the above drawback can be overcome.

It has appeared that lubricating oils in

sulphonated according to the process of the invention alkylsalicylic acids and alkylphenols, both containing at least one alkyl group with at least 12 carbon atoms, can be mixed. Preferably, for the preparation of alkylsalicylic acids the said mixtures are obtained as such, and it is preferred to sulphonate such a mixture. This process for the preparation of alkylsalicylic acids consists in that alkali metal salts of alkylphenols containing at least one alkyl group with at least 12 carbon atoms are treated with carbon dioxide at a temperature of 110—160° C and, preferably, at a pressure of 10—30 atm. (the pressures referred to herein are absolute pressures), and the salts of alkyl phenols and alkylsalicylic acids present in the mixture obtained are converted to alkylphenols and alkylsalicylic acids with the aid of a mineral acid.

The sulphonation of the mixture thus obtained is particularly advantageous in that use is made of alkylphenols which have not been converted to alkylsalicylic acids, and which would not have a useful function if, as

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PATENT SPECIFICATION

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C5F 524 631 762 A

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(54) LUBRICANT ADDITIVES

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the preparation of a lubricant additive, a process for the preparation of concentrates of a lubricant additive and to a process for the preparation of lubricant compositions. The invention also relates to lubricant additives, concentrates and lubricant compositions obtained according to the said processes.

Lubricating oils in which as an additive a salt of an alkylsalicylic acid containing at least one alkyl group with at least 12 carbon atoms and an alkaline earth metal, in particular calcium is present, have been used for many years in engines, in particular diesel engines. These additives have dispersing properties enabling them to keep the internals of engine cylinders clean and to counteract the deposition of carbonaceous products on pistons and in ring grooves, ring-sticking thus being prevented.

Recently the said lubricating oils have increasingly been used in gasoline engines. It has been found that in gasoline engines the protection against rusting, with lubricating oils which contain the said salts of alkylsalicylic acids, is not in all cases completely adequate. Consequently, lubricant additives have been searched for by which the above drawback can be overcome.

It has appeared that lubricating oils in which mixtures of salts of alkylsalicylic acids, is not in all cases completely adequate. Consequently, lubricant additives have been searched for by which the above drawback can be overcome.

It has appeared that lubricating oils in

which mixtures of salts of alkylsalicylic acids and alkylphenolsulphonic acids (both types of acid at least containing one alkyl group with at least 12 carbon atoms), are present, have a very beneficial influence on rusting in gasoline engines. A simple and effective method for the preparation of these mixtures has now been found.

According to the invention there is provided a process for the preparation of a lubricant additive which comprises sulphonating alkylphenols containing at least one alkyl group with at least 12 carbon atoms in the presence of alkylsalicylic acids containing at least one alkyl group with at least 12 carbon atoms, and converting, by any known method, the alkylsalicylic acids and alkylphenolsulphonic acids present in the mixture obtained to salts of one or more polyvalent metals.

For the preparation of the mixtures to be sulphonated according to the process of the invention alkylsalicylic acids and alkylphenols, both containing at least one alkyl group with at least 12 carbon atoms, can be mixed. Preferably, for the preparation of alkylsalicylic acids the said mixtures are obtained as such, and it is preferred to sulphonate such a mixture. This process for the preparation of alkylsalicylic acids consists in that alkali metal salts of alkylphenols containing at least one alkyl group with at least 12 carbon atoms are treated with carbon dioxide at a temperature of 110—160° C and, preferably, at a pressure of 10—30 atm. (the pressures referred to herein are absolute pressures), and the salts of alkyl phenols and alkylsalicylic acids present in the mixture obtained are converted to alkylphenols and alkylsalicylic acids with the aid of a mineral acid.

The sulphonation of the mixture thus obtained is particularly advantageous in that use is made of alkylphenols which have not been converted to alkylsalicylic acids, and which would not have a useful function if, as

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usual, the alkylsalicylic acids present in such mixtures were converted to salts of a polyvalent metal and these salts were used as lubricant additives. Therefore, in the preferred process no larger amount of alkylphenols is required for the preparation of a lubricant additive according to the invention than previously for the preparation of a lubricant additive which afforded less protection against rusting.

In order to obtain an optimal engine cleanliness performance of the additives according to the invention, it is particularly advantageous that the alkylphenols containing an alkyl group with at least 12 carbon atoms, as well as the alkylphenols from which the alkylsalicylic acids have been prepared, should to an extent of at least 60 %m consist of alkylphenols in which an alkyl group is present which is bound to the benzene nucleus in the para-position with respect to the hydroxyl group.

Preference is given to alkylphenols of which the greater part of the molecules contain two alkyl groups bound to the benzene nucleus, at least one of which has at least 12 carbon atoms. Preferably, one of the alkyl groups is a tertiary butyl group. For the preparation of alkylsalicylic acids these alkyl groups should be attached to the benzene nucleus in such a way that at least one ortho-position is free (so for instance be attached to one ortho-position and the para-position). For the preparation of alkylphenolsulphonic acids the position to which the alkyl groups are attached to the benzene nucleus does not play a dominating part. In general, the alkylphenols do not carry an alkyl substituent in the meta-positions.

Very suitably at least part of the alkyl groups which are bound to the benzene nucleus in the para-position with respect to the hydroxyl group are bound to the benzene nucleus of a quaternary carbon atom.

The alkylphenols can for instance, be prepared by alkylation, using phenol, ortho-alkylphenol or para-alkylphenol as starting material, an olefin or a mixture of olefins with more than 12 carbon atoms in the molecules very suitably being used as the alkylation agent. Acid-activated clays have proved very suitable as catalysts in the alkylation of phenol, orthoalkylphenol and para-alkylphenol. The amount of catalyst used generally amounts to 1—10 %w, in particular 3—7 %w, calculated on the total amounts by weight of alkylation agent and phenol to be alkylated.

The alkylation can e.g. be carried out at temperatures between 100° and 225° C.

If non-substituted phenol is alkylated in one step with olefins having at least 12 carbon atoms, preferably 2—4 mole of olefins per mole of phenol is used, particularly 2.5—3.0 mole of olefins per mole of phenol.

If ortho-alkylphenol or para-alkylphenol is

alkylated, preferably 0.5—1.0 mole of olefin per mole of ortho-alkylphenol or para-alkylphenol is used, particularly 0.7—0.8 mole of olefin per mole of ortho-alkylphenol or para-alkylphenol. Very satisfactory results are obtained if as starting material for the synthesis ortho-cresol or para-cresol is used.

The preparation of alkylphenols containing an alkyl group with at least 12 carbon atoms and an alkyl group which is bound to the benzene nucleus by a quaternary carbon atom is very suitably carried out by the alkylation of non-substituted phenol in 2 steps with the use of a different alkylation agent in each step, one of which is a tertiary alkylation agent having at most 12 carbon atoms in the molecule, and the other an alkylation agent having at least 12 carbon atoms. Preference is given to the catalysts and temperature ranges as described hereinbefore. Examples of suitable tertiary alkylation agents are here monoolefins having at most 11 carbon atoms in the molecule, of which one carbon atom with a double bond carries a side chain or both carbon atoms with a double bond carry a side chain. Monoolefins having the general formula



in which R represents an alkyl group with at most 8 carbon atoms, such as isopentene and isohexene, and in particular isobutene, are very suitable.

Examples of olefins with at least 12 carbon atoms which can be used as alkylation agents are unbranched monoolefins with at least 12 carbon atoms in the molecule. Technical mixtures of unbranched monoolefins having more than 12 carbon atoms in the molecule, in particular technical olefins having more than 12 carbon atoms, more is particular 14—18 carbon atoms in the molecule, which have been prepared by cracking of unbranched paraffins obtained by means of urea extraction, are very suitable.

The sulphonation of the mixture of alkylsalicylic acids and alkylphenols can be carried out in any desired way, for instance with the aid of sulphur trioxide. Preference is given to sulphonation with sulphuric acid containing at most 25 %w of water, and particularly from 0 to 10 %w of water. Fuming sulphuric acid can also be used. With the use of sulphuric acid, whether diluted or not, the sulphonation is very suitably carried out at a temperature of 20—60° C with stirring. The quantity of sulphuric acid can vary between wide limits. Molar ratios of sulphuric acid to the alkylphenols present in the mixture between 1:1 and 1:10 are very suitable, a less than the theoretical quantity of sulphuric acid can also be used.

If desired the sulphonation can be carried out in a solvent, which naturally must not

take part in the sulphonation reaction. Aliphatic hydrocarbons, for instance heptane or hexane, are very useful; aromatic hydrocarbons such as xylene can be used, provided that such a low sulphonation temperature is selected that substantially no sulphonation of the aromatic hydrocarbon occurs.

It is possible to carry out the conversion of a mixture of salts of alkylphenols and alkylsalicylic acids (for instance the mixture obtained in the treatment of alkali metal salts of alkylphenols containing at least one alkyl group with at least 12 carbon atoms, with carbon dioxide at a temperature of 110—160° C and, preferably, at a pressure of 10—30 atm as described hereinbefore) and the sulphonation in one step by treating the said mixture with sulphuric acid. The salts of the alkylphenols and alkylsalicylic acids are then first converted to the respective acids and subsequently the alkylphenols are sulphonated. In this process considerable quantities of alkali metal sulphate, for example, sodium sulphate are formed, which may give rise to the formation of a slurry. For this reason it is preferred to convert the mixture of salts of alkylphenols and alkylsalicylic acids to the free alkylphenols and alkylsalicylic acids with the aid of dilute mineral acid, and to remove the inorganic salts formed before sulphonation.

It has been found that in the sulphonation of a mixture of alkylphenols and alkylsalicylic acids sulphonic acid groups are introduced into the alkylphenols, the alkylsalicylic acids in the mixture remaining completely or substantially unchanged.

After sulphonation the excess of sulphuric acid is to be removed. This can very suitably be done by decantation after separation of the layers. If desired, the mixture can be diluted with an organic solvent, for instance hexane or heptane, prior to layer separation.

According to the invention the alkylsalicylic acids and alkylphenolsulphonic acids present in the mixture obtained are converted to salts of polyvalent metals. As metals zinc or chromium may for instance be used, but preference is given to alkaline earth metals, particularly calcium, because the salts obtained with alkaline earth metals are very suitable as lubricant additives.

Preference is given to the preparation of basic salts. By the term "a basic salt of a polyvalent metal and an alkylsalicylic acid and/or an alkylphenolsulphonic acid", as used in the description and claims of the present patent application, must be understood to mean a compound of a polyvalent metal or a mixture of compounds of polyvalent metals containing, besides the polyvalent metal, one or more acid radicals of alkylsalicylic acids and/or alkylphenolsulphonic acids and in which the number of gram equivalents of polyvalent metal is larger than

the number of gram equivalents of alkylsalicylic acid+alkylphenolsulphonic acid. The basicity of such salts of polyvalent metals can be expressed in the formula

$$\frac{M}{Z} (\frac{M}{Z} - 1) \times 100\%, \quad 70$$

in which M represents the number of equivalents of polyvalent metal and Z the number of equivalents of alkylsalicylic acid+alkylphenolsulphonic acid, for instance per 100 g of the basic metal salt. A basicity of the polyvalent metal salts up to about 1000% is generally feasible.

A basicity of up to about 250%, for instance between 25 and 225%, is preferred if the basic salt is used as lubricant additive.

The preparation of neutral and basic salts of polyvalent metals from these alkylsalicylic acids and alkylphenolsulphonic acids can be carried out in accordance with any known method; methods for this conversion have been described in the literature. For instance, for the preparation of neutral calcium salts the alkylsalicylic acids and alkylphenolsulphonic acids can be converted to the corresponding sodium salts and the latter can be caused to react with an equivalent quantity of CaCl_2 .

For the preparation of basic calcium salts with a relatively low basicity, for instance 50%, the alkylsalicylic acids and alkylphenolsulphonic acids can be treated with an excess of calcium in the form of Ca(OH)_2 . For the preparation of basic calcium salts with a higher basicity, for instance 200%, the alkylphenolsulphonic acids and alkylsalicylic acids, dissolved in a hydrocarbon/alcohol mixture, preferably a xylene/methanol mixture, can be treated with carbon dioxide in the presence of a hydroxide of a polyvalent metal, for instance about 4 equivalents of calcium in the form of Ca(OH)_2 , with introduction of about 1.6 equivalents of CO_2 .

The lubricant additive obtained according to the process of the invention can very suitably be incorporated into a lubricating oil. In general preference is given to such a quantity that the lubricating oil has a total polyvalent-metal content of 0.05—1 %w (determined as sulphated ash according to ASTM method D 874).

Generally the ratio between the quantities of alkylphenol sulphonic acids and alkylsalicylic acids, obtained by sulphonation of a mixture resulting from the preparation of alkylsalicylic acids as described above, need not be at an optimum for the use in a lubricant of salts of polyvalent metals of the alkylphenolsulphonic acids and the alkylsalicylic acids present in that mixture. If it is felt that the said ratio is too high, it can be reduced by incorporation into the lubricant

of a mixture of salts of a polyvalent metal (such as an alkaline earth metal, particularly calcium) of alkylsalicylic acids. These salts can for instance be obtained by conversion of the alkylsalicylic acids present in a mixture of alkylsalicylic acids and alkylphenols, both containing at least one alkyl group with at least 12 carbon atoms, which is very suitably a similar mixture to that used in the sulphonation, to salts of a polyvalent metal, preferably basic salts.

When the last-mentioned type of salts is also incorporated into a lubricant, the ratio of the quantity of alkylphenolsulphonic acid to the quantity of alkylsalicylic acid is lower than when the lubricant additive according to the invention is exclusively present in the lubricant, provided the amount of polyvalent metal in the lubricant is kept constant. In general salts of polyvalent metals of mixtures of alkylphenolsulphonic acids and alkylsalicylic acids containing 5 to 25 %m of alkylphenolsulphonic acids, calculated on the total amount of the said acids, are very suitable to impart a good antirust performance to a lubricating oil.

Besides in lubricating oils, which may be of mineral or synthetic origin (and may also consist of mixtures of these type of lubricating oil, for instance a mixture of a mineral oil and an ester oil), the lubricant additives according to the invention can also suitably be used in lubricating greases.

Besides in lubricating oils, which may be of mineral or synthetic origin (and may also consist of mixtures of these types of lubricating oil, for instance, a mixture of a mineral oil and an ester oil), the lubricant additives according to the invention can also suitably be used in lubricating greases.

The lubricant additives obtained according to the process of the invention are particularly suitable to improve the quality of mineral lubricating oils or mixtures thereof. These lubricant additives can be incorporated into the lubricant as such, or in the form of a concentrate which for instance has been obtained by mixing the lubricant additive according to the invention with a small quantity of mineral oil. Salts of alkylsalicylic

acids (for instance obtained by converting a mixture of alkylphenols and alkylsalicylic acids to basic salts) can also be incorporated into such a concentrate, in order to adjust the ratio of alkylphenolsulphonic acids to alkylsalicylic acids in the concentrate to the value ultimately desired in the lubricant. A metal content of the concentrates of 3—5%, determined as sulphated ash, is very suitable.

Besides the lubricant additives obtained according to the invention, lubricant compositions according to the invention may contain other additives, such as antioxidants, foam inhibitors, anti-corrosion additives, viscosity improvers and/or viscosity index improvers (such as hydrogenated copolymers of conjugated dienes and(alkyl)-styrenes), lubricity improvers and other substances which are usually added to lubricants.

EXAMPLE

Phenol was alkylated at 200° C with a C_{10} — C_{18} olefins mixture (molar ratio 1.3:1) using 5 %w acid-activated clay as the catalyst. The alkylphenols thus obtained were subsequently alkylated at 150° C with isobutene (molar ratio 1:1.1), again using 5 %w acid-activated clay as the catalyst. The volatile components were removed by distillation, finally under vacuum up to a final pressure of 20 mm mercury and a bottom temperature of 228° C. The alkphenols obtained were diluted with the same amount by weight of xylene and subsequently converted to alkylphenates with sodium (10% excess on hydroxyl number). Then 400 pbw of this solution was treated with 31.2 parts by weight of CO_2 at a pressure of 35 atm and a temperature of 140—145° C for 6 hours. The product obtained was converted to a mixture of alkylphenols and alkylsalicylic acids with the aid of 165 pbw of 10% HCl at 80° C, and this mixture was washed with water till it was free of ionic chlorine.

The mixture obtained had the composition given in the table set forth hereinafter as Table I. The alkylsalicylic acids were a mixture of:—

5 %m 3 - (C_{10} — C_{18})alkylsalicylic acid	} 95 %m substituted in the para-position
24 %m 5 - (C_{10} — C_{18})alkylsalicylic acid	
9 %m 3.5 - di(C_{10} — C_{18})dialkylsalicylic acid	
38 %m 3 - (C_{10} — C_{18})alkyl - 5 - tert - butylsalicylic acid	
24 %m 3 - (tert - butyl - 5 - (C_{10} — C_{18}) alkylsalicylic acid	

The washed mixture (300 pbw) was sulphonated at 40° C by addition of 40 pbw of 95% sulphuric acid in 30 minutes with stirring, and subsequently stirring for one more hour at 40° C. The mixture was then diluted with 240 pbw of hexane and the layers were separated. The hexane was evaporated off

at the bottom temperature of at most 100° C. The composition of the mixture obtained is given in Table I. The weight of this mixture amounted to 287 pbw, the acid number was 1.61 (meq/g).

Subsequently 300 pbw of xylene, 60 pbw of methanol and 67.6 pbw of $Ca(OH)_2$ were

added, and 16.6 pbw of CO₂ introduced at 40—50° C with stirring. The methanol and water were distilled off. The product obtained was a 200% basic calcium salt of a mixture of alkylphenolsulphonic acids and alkylsalicylic acids. The quantity of alkylphenolsulphonic acids present amounted to 30% of the total acid.

Concentrates in oil were prepared containing 4.5% calcium and the quantities of alkylphenolsulphonic acids indicated in Table II, calculated on alkylphenolsulphonic acids+alkylsalicylic acids, by mixing the obtained mixture of 200% basic salts of alkylphenolsulphonic acids and alkylsalicylic acids with a 200% basic calcium salt of alkylsalicylic acids obtained by conversion of the alkylsalicylic acids to 200% basic salts in a mixture similar to that subjected to sulphonation.

Of the concentrates such an amount was incorporated into a mineral lubricating oil with a viscosity of 11.4 cSt at 99° C, which had been obtained from a crude oil originating from the Middle East, that the calcium content, determined as sulphated ash, amounts to 0.15%. These lubricating oil compositions were tested in a "Caterpillar" diesel engine.

Such an amount of the concentrates was incorporated into a second lubricating oil obtained from a crude mineral oil originating from the Middle East and having a viscosity of 4.8 cSt at 99° C that the calcium content, determined as sulphate ash, amounted to 0.18%. Also incorporated into this lubricating oil was 3.5 %w of an imide of an

alkenylsuccinic acid and a polyalkylenepolyamine, 1.1 %w of a zincdialkyl dithiophosphate and 0.25 %w of an alkylphenoxytetraethoxyethanol. This lubricating oil composition was tested in a Ford "Cortina" 1500 gasoline engine (Cortina is a Registered Trade Mark).

The "Caterpillar" engine was a one-cylinder four-stroke diesel engine cooled with ethylene glycol; bore 5 1/8 inches; stroke 6 1/2 inches. The test conditions were: 1800 rev/min; load: 45 hp; temperature of the cooling liquid: 85° C; oil temperature: 95° C; intake-air temperature: 45° C; intake pressure: 1340 mm Hg abs.; quantity of lubricating oil tested: 5000 g; fuel: gasoline with about 1 %w of sulphur; test period: 48 hours.

In this test the degree of piston fouling is expressed in a scale of 0—100 (10 is clean).

The Ford "Cortina" 1500 engine was a four-cylinder four-stroke gasoline engine; bore: 3.18 inches; stroke: 2.8 inches. The test conditions were: velocity: 2000 rev/min; load: 6 hp; carter oil temperature: 60° C. The blow-by gas was condensed and recycled to the engine. The rocker box cover was cooled and below the rocker box cover 4 mild steel sheets were mounted. The test period was 48 hours. The degree of rusting was determined by measuring the weight loss of the push rods, the oil dipstick and the said mild steel sheets. The results of the engine tests are presented in Table II.

TABLE I

	Before sulphonation, %w	After sulphonation, %w
Alkylsalicylic acids	49	47
Alkylphenolsulphonic acids	—	22
Monoalkylphenols	0	0
Dialkylphenols	23	10
Trialkylphenols	14	4
Hydrocarbons (polymerized olefins)	14	17

TABLE II

Test No.	Alkylphenolsulphonic acid, %w	Fouling of pistons of "Caterpillar"*	Ford "Cortina" (weight loss, mg)**
1	0	+0.6	305
2	8.8	+0.1	180
3	12	+0.8	139
4	16	+1.1	120
5	20	—	85

*Difference in degree of fouling of piston between the oil tested and a commercial oil based on basic calcium salts of alkylsalicylic acids.

**Total weight loss of push rods, oil dipstick and mild steel sheets mounted below the rocker box cover.

Table II shows that the oil compositions according to the invention cause a decrease of the weight loss as a result of rusting in the Ford "Cortina" 1500 engine, while quantities of alkylphenolsulphonic acids larger than about 10 %w give rise to a lower degree of fouling of the piston in the "Caterpillar" engine than without alkylphenolsulphonic acids being used.

10 WHAT WE CLAIM IS:—

1. A process for the preparation of a lubricant additive, which comprises sulphonating alkylphenols containing at least one alkyl group with at least 12 carbon atoms in the presence of alkylsalicylic acids containing at least one alkyl group with at least 12 carbon atoms, and converting, by any known method, the alkylsalicylic acids and alkylphenolsulphonic acids present in the mixture obtained to salts of one or more polyvalent metals.

2. A process according to claim 1, in which a mixture is sulphonated which has been obtained by treating alkali metal salts of alkylphenols containing at least one alkyl group with at least 12 carbon atoms with carbon dioxide at a temperature of 110—160° C and a pressure of 10—30 atm, and converting the salts of alkylphenols and alkylsalicylic acids with the aid of a mineral acid.

3. A process according to claim 1 or 2, in which the alkylphenols containing an alkyl group with at least 12 carbon atoms consist to an extent of at least 60 %m of alkylphenols containing an alkyl group which is bound to the benzene nucleus in the para-position with respect to the hydroxyl group.

4. A process according to claim 3, in which at least part of the alkyl groups which are bound to the benzene nucleus in the para-position with respect to the hydroxyl group are bound to the benzene nucleus by a quaternary carbon atom.

5. A process according to any one of the preceding claims, in which the greater part of the molecules of the alkylphenols containing at least one alkyl group with at least 12 carbon atoms contain two alkyl groups bound to the benzene nucleus.

6. A process according to claim 5, in which one of the alkyl groups is a tertiary butyl group.

7. A process according to any one of the preceding claims, in which the alkyl groups with at least 12 carbon atoms have 14—18 carbon atoms.

8. A process according to any one of the preceding claims, in which the sulphonation is carried out with sulphuric acid containing at most 25 %w of water.

9. A process according to claim 8, in which the sulphonation is carried out with sulphuric acid containing 0—10 %w of water.

10. A process according to claim 8 or 9,

in which the sulphonation is carried out at a temperature of 20—60° C.

11. A process according to any one of the preceding claims, in which the alkylsalicylic acids and alkylphenolsulphonic acids present in the mixture obtained after sulphonation are converted to basic salts of one or more polyvalent metals (as hereinbefore defined).

12. A process according to claim 11, in which the alkylsalicylic acids and alkylphenolsulphonic acids present in the mixture obtained are converted to salts having a basicity (as hereinbefore defined) of between 25 and 225 %.

13. A process according to any one of the preceding claims, in which the polyvalent metals are alkaline earth metals.

14. A process according to claim 13, in which calcium is used as alkaline earth metal.

15. A process according to any one of claims 11—14, in which the conversion of the alkylsalicylic acids and the alkylphenolsulphonic acids to the higher basicity salts of polyvalent metals is carried out by treating these acids with carbon dioxide in a solution of a hydrocarbon/alcohol mixture in the presence of a hydroxide of a polyvalent metal.

16. A process according to claim 15, in which the hydrocarbon/alcohol mixture is a xylene/methanol mixture and the hydroxide is calcium hydroxide.

17. Lubrication additives whenever obtained according to the process of any one of the preceding claims.

18. A process for the preparation of a lubricant composition, in which a lubricant additive according to claim 17 is incorporated into a lubricant.

19. A process according to claim 18, in which the lubricant is a mineral lubricating oil.

20. A process according to claim 18 or 19, in which a mixture of compounds, obtained by conversion of the alkylsalicylic acids present in a mixture of alkylphenols both containing at least one alkyl group with at least 12 carbon atoms and alkylsalicylic acids containing at least one alkyl group with at least 12 carbon atoms, to basic salts of a polyvalent metal, is also incorporated into the lubricant.

21. A process according to any one of claims 18—20, in which the polyvalent metal is an alkaline earth metal.

22. A process according to claim 20 or 21, in which the quantity of alkylsulphonic acid amounts to 5—25 %m of the total quantities of alkylphenolsulphonic acid and alkylsalicylic acid together.

23. A process according to any one of claims 18—22, in which the total polyvalent metal content of the lubricant composition (determined as sulphated ash) amounts to 0.05—1 %w.

24. Lubricant compositions whenever ob-

tained according to the process of any one of claims 18—23.

5 25. A process for the preparation of concentrates, in which such an amount of lubricant additive according to claim 17 is incorporated into a mineral oil that the polyvalent-metal content amounts to 3—5 %w (determined as sulphated ash).

10 26. A process for the preparation of concentrates, in which such an amount of lubricant additive according to claim 17 and such an amount of a basic salt of an alkylsalicylic acid containing at least one alkyl group with at least 12 carbon atoms are incorporated into a mineral oil that the quantity of alkyl-

15 phenolsulphonic acid amounts to 5—25 %m

of the total quantities of alkylphenolsulphonic acid and alkylsalicylic acid together, and the polyvalent-metal content (determined as sulphated ash) amounts to 3—5 %w.

27. Concentrates whenever obtained according to the process of claim 25 or 26.

28. A process according to claim 1, substantially as described with special reference to the Example.

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